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BIO-ASSAY INVESTIGATIONS BUFFALO RIVER, BUFFALO, NEW YORK

Croswell Henderson, et al

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

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BIO-ASSAY INVESTIGATIONS

BUFFALO RIVER

BUFFALO, NEW YORK

Prepared by

Croswell Henderson, Biologist

Sanitary Engineering Center, USPHS

Cincinnati, Ohio

and

H. A. Anderson, Public Health Engineer

I.J.C. Field Unit, USPHS

Buffalo, New York

INTRODUCTION

Purpose

In January 1956, field studies were initiated on a cooperative basis to determine the possible effects of industrial wastes from major Buffalo River industries on the eastern end of Lake Erie and the Niagara River. Buffalo River industries cooperating in this project were the National Aniline Division - Allied Chemical and Dye Corporation, Donner-Hanna Coke Corporation, and Socony-Mobil Oil Company.

This report covers an investigation of the toxicity to fish of Buffalo River water under different flow conditions at various seasons of the year.

Industrial wastes known to be significantly toxic to aquatic life are discharged into the Buffalo River at several points. These chemically complex wastes when mixed with each other or when under the influence of non-toxic components in the wastes or receiving water, may exert an entirely different

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toxicity from that of a single waste. Reactions such as hydrolysis, precipitation, complexing, biological and/or chemical oxidation, loss of volatiles, etc., may occur and change the toxicity picture greatly.

The Buffalo River has been classified by the New York Water Control Board into a category which does not require the protection of aquatic life. This river, however, enters Lake Erie and the Niagara River, waters in which aquatic life protection is required.

Bio-assays were thus made to determine directly the toxicity of Buffalo River water and to evaluate the possible effects on aquatic life in the receiving waters.

Personnel Participating

Erie County Health Department

M. J. Stankewich, Principal Engineer

Everett Sommerfeldt, Sanitary Engineer

Public Health Service

H. H. Black, Industrial Wastes Consultant

Dr. C. M. Tarzwell, Chief, Aquatic Biology Unit

Croswell Henderson, Aquatic Biologist

H. A. Anderson, Public Health Engineer

M. W. Ruszaj, Chemist

Organization of Study

Bio-assays were conducted on Buffalo River water samples during the same periods that similar studies were being made on industrial effluents.

Samples of river intake water were collected by the industries and

samples at several downstream stations were collected by Erie County Health Department personnel.

The Public Health Service conducted bio-assays in laboratory space provided by National Aniline Division in Buffalo. Analyses for phenols and cyanides were made in the Buffalo I.J.C. Unit Laboratory.

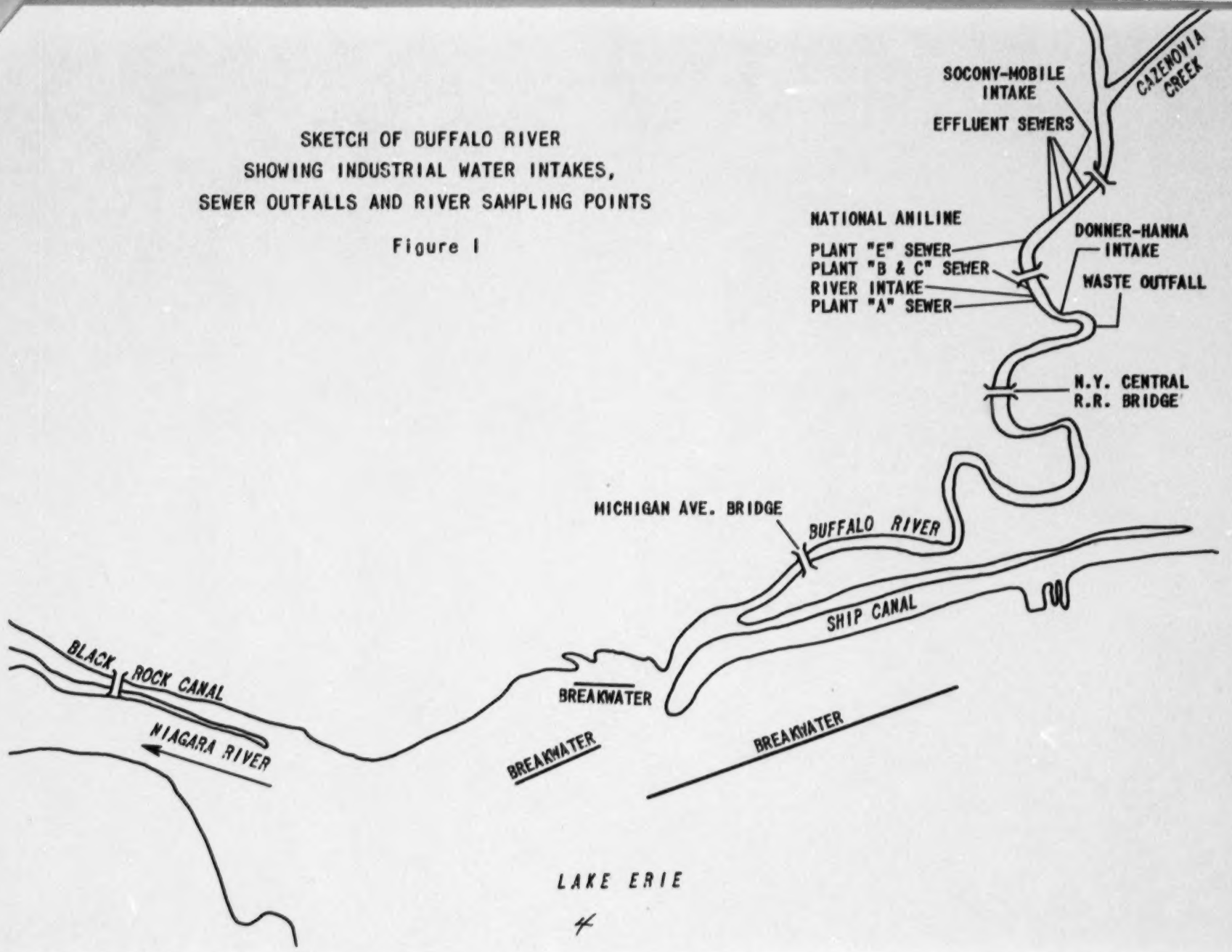
GENERAL INFORMATION

The Buffalo River is formed by the junction of three small streams, Cayuga, Cazenovia, and Buffalo Creeks. From the entrance of Cazenovia Creek, the river takes a meandering course for approximately five miles through an industrial section of Buffalo where it enters the eastern end of Lake Erie, a short distance from the beginning of the Niagara River (Figure 1). Depending on river stages, prevailing winds and lake levels, wastes entering the Buffalo River may be transported to the Niagara River within relatively short time periods.

The Buffalo River has been enlarged for navigation by dredging to a channel approximately 300 feet wide and 20 feet deep. This channel extends from the mouth to a point upstream from the Socony-Mobil Oil Company refinery and includes all of the section investigated during this survey.

SKETCH OF BUFFALO RIVER
SHOWING INDUSTRIAL WATER INTAKES,
SEWER OUTFALLS AND RIVER SAMPLING POINTS

Figure 1



Flows in the Buffalo River have been reported to range from a low of 10 cfs to as much as 27,000 cfs for short periods following heavy rainfall. Normally, high flows occur during the winter and spring months while low flows occur in the summer and fall.

Based on a USGS report, the following flows may be expected:

12 cfs may be exceeded 99% of the time.

48 cfs may be exceeded 80% of the time.

105 cfs may be exceeded 60% of the time.

242 cfs may be exceeded 40% of the time.

During 1952 industrial use averaged 193 cfs. During summer, industrial use may approach 286 cfs or about 30 times minimum flow.

During low flow periods water may be recirculated through industrial plants several times from what is in reality a long, narrow pool. The flow in the Buffalo River is subject to rapid fluctuation from heavy rains. Waste materials that may have been concentrated in this pool may be flushed into Lake Erie and the Niagara River with possible detriment to aquatic life.

While the three industries studied were expected to be the major contributors to toxic wastes in the Buffalo River basin, other industries were known to contribute wastes, some of which were highly acid and others with high oxygen demand. Municipalities are known to contribute raw sewage which also has oxygen demand. Barge traffic in the channel may contribute to the oil pollution. Especially during periods of low flow, the Buffalo River may serve as a treatment basin for wastes subject to biological oxidation or other means of natural purification. The amount of dilution water available for assimilation of wastes depends on levels in Lake Erie as well as upon

Buffalo River tributary flows. Dilution of river water with Lake Erie water occurs for some distance upstream during periods of reversal of flow. On at least one occasion when strong winds were prevalent, Buffalo River water levels rose considerably (six feet or more at the National Aniline intake) and were greatly detoxified even though tributary flows remained at low levels.

Waste Control Measures

In addition to the waste control measures carried out by individual industries, the National Aniline Division adds sufficient lime to the Buffalo River during periods of low flow to maintain a pH of 6 or greater in the river water.

SURVEY METHODS

Sampling

The Buffalo River sampling stations used during some or all periods of this study as well as some of the major outfalls are shown in Figure 1. Sampling stations in order of decreasing distances from the river mouth were as follows:

Station No.	Location
1	Socony-Mobil Oil Company intake
2	National Aniline Division intake
3	Donner-Hanna Coke Corporation (Republic Steel Co.) intake
4	New York Central Railroad Bridge
5	Michigan Avenue Bridge

Socony-Mobil and Donner-Hanna intake waters were collected hourly and composited over an 8-hour period. National Aniline intake water was sampled continuously to provide a 24-hour composite.

Samples at the New York Central and Michigan Avenue bridges were collected hourly from mid and quarter points at 8 foot depth and composited over a 4-hour period. Preliminary investigation, based on the distribution of chlorides, established that the upstream wastes were uniformly distributed in the Buffalo River at Michigan Avenue bridge.

Chemical Methods

All chemical determinations were made according to procedures given in "Standard Methods for the Examination of Water, Sewage, and Industrial Wastes," 10th Edition, published by the American Public Health Association.

Bio-assay Methods

Bio-assays were made, essentially, by the method recommended by the toxicity subcommittee of the Federation of Sewage and Industrial Wastes Associations (Sewage and Industrial Wastes, Vol. 23, No. 11, 1380, Nov. 1951). This method consists of preparing various concentrations of effluent in a selected dilution water, adding the test fish and observing their reactions over a definite time period. A logarithmic series of numbers is generally most convenient for preparing different test concentrations.

As the river water samples were of unknown toxicity, exploratory or small scale tests were made to determine the approximate toxic range. Test solutions were prepared over a wide range of concentrations (e.g. 100, 10, and

1 per cent effluent). Two fish were added to 2 liters of each concentration in 6-1/2 inch diameter, 1 gallon wide mouth glass bottles. Observations for relatively short time periods indicated test concentrations necessary for the full scale experiments.

In the full scale tests, 10 fish were generally used for each test concentration. Five fish were added to 10 liter duplicate samples in 10 inch diameter, 5 gallon widemouth glass bottles. The intermediate concentrations tested were dependent upon information obtained from the exploratory tests. For example, if fish were killed in concentrations of 100 per cent and not affected in concentrations of 10 per cent, intermediates were set up within this range, 100, 56, 32, 18, and 10 per cent concentration of river water.

The dilution water used was raw Lake Erie water obtained at the Buffalo, New York, water plant. This water was hauled into the laboratory, allowed to come to room temperature, and aerated vigorously for at least one hour to bring it to equilibrium with atmospheric gases. Characteristics of this water at time of use were as follows: Dissolved oxygen 7.6-8.2 ppm; pH 8.0-8.2; Total alkalinity ($CaCO_3$) 94-100 ppm; Total acidity ($CaCO_3$) 0.1 ppm; Versenate hardness ($CaCO_3$) 120-135 ppm.

The test fish used were fathead minnows (Pimephales promelas) of a fairly uniform size, ranging in length from 2 to 2-1/2 inches and in weight from 1 to 1-1/2 grams. These fish were obtained in uniform lots from the Newtown, Ohio, Fish Hatchery and acclimated to laboratory conditions. This species is of intermediate tolerance to chemicals comparable to bass, sunfish, perch, and other warm water species, and will tolerate fairly low oxygen conditions (1-2 ppm).

Another species, the emerald shiner (Notropis atherinoides), obtained locally from a Buffalo bait dealer, was used in some experiments in order to obtain a comparison of the toxicity to fatheads and this locally abundant species.

The bio-assays were made at ordinary laboratory temperatures which were within the range from 22 to 25° C. and would compare favorably with maximum summer water temperatures in this area.

The tests were designed so that no oxygenation or aeration was generally needed. Absorption of atmospheric oxygen by the exposed water surface was normally adequate for fish requirements during the test period. However, in some of the bio-assays, high oxygen demand samples caused oxygen depletion. When necessary, oxygen was maintained by bubbling pure oxygen through the test solution by means of a suitable arrangement of valves and small tubing. The rate (60-180 bubbles per minute) was adjusted to maintain adequate oxygen for fish survival with minimum agitation in order to prevent the loss of volatile materials.

Physical and chemical determinations (temperature, dissolved oxygen, pH, alkalinity, and hardness) were made on each concentration initially, and after fish mortality, or at the completion of the test. This was done primarily to maintain control of oxygen conditions and to differentiate between fish mortality due to oxygen deficiency or acidity and toxic properties.

Fish reactions were observed over a 96 hour period. From the mortality in the different concentrations, 24, 48, and 96 hour TL_m (Median tolerance limit) values were obtained. The median tolerance limit is the concentration of river water in Lake Erie dilution water that kills just 50 per cent of the

test fish. These values were obtained by straight line graphical interpolation from points representing per cent survival of fish and log concentrations of effluents which bracketed the 50 per cent point.

As river water samples were of relatively low toxicity, high test concentrations were usually necessary. The samples were not tested until remaining in the laboratory long enough for room temperature to be reached. Dissolved oxygen was low in some samples and in those it was necessary to add oxygen before beginning the bio-assays .

RESULTS

Hydrologic Data

The U. S. Geological Survey maintains gauging stations on the three tributaries of the Buffalo above points where any effect would be manifest from Lake Erie levels. The flows of the Buffalo River for the periods of this study, Table 1, were determined by summing the discharges at the three gauging stations, obtained from the Geological Survey. The mean flows for each sampling period are also shown.

Minimum flows occurred in June with somewhat higher flows in January and November and much higher flows in February and March. A special effort was made to conduct bio-assays during a period of minimum flow. The June flows were apparently the lowest during 1956. These values, however, were much higher than some of the minimum values for previous years, which have been reported as low as 10 cfs. The mean monthly flow for July 1955, was 14 cfs with minimum daily flows as low as 5 cfs. No bio-assays were made during any extremely high flow periods.

TABLE 1 - BUFFALO RIVER FLOWS DURING VARIOUS SAMPLING PERIODS IN CFS

USGS DATA

	January	February	March	June	November
4					
5					99
6					87
7					82
8					83
9					82
10					77
11					73
12		1162	1574		76
13		896	960		80
14		717	981		90
15		1510	690		87
16	204	1194	645		86
17	192	826	810	76	81
18	93	1410	690	76	
19	98	1620	585	68	
20	91	1030	534	62	
21	119	770	513	56	
22	134	497	473	56	
23	119	465	457	49	
24	104	354		63	
25	90			72	
26	83			56	
27	90			50	
28				44	
29				43	
AVERAGE	118	958	743	59	83
RANGE	(83-204)	(354-1620)	(457-1574)	(43-76)	(73-99)

The water levels in Lake Erie at Buffalo during 1956, are shown in Table 1A. While Lake Erie levels were not definitely correlated with Buffalo River flows and toxicity, observations in November indicated a large reduction in toxicity at Station 3, when Lake Erie levels were quite high. High lake levels increase greatly the dilution water available in the Buffalo basin. Reversal of flow in the Buffalo River was observed on several occasions. Even at low lake levels, there is apparently some additional dilution at least as far upstream as Station 5, as indicated by both physical and chemical characteristics and toxicity.

Mean monthly flows in the Niagara River are shown in Table 1B. Because of the tendency for Buffalo River discharge to follow the east shore, only a small portion of Niagara River flow is available for immediate dilution.

Physical and Chemical Characteristics

A general description and some of the chemical characteristics of Buffalo River waters at the various sampling stations during the different seasons are shown in Table 2.

The waters of the Buffalo River in the study section varied from a turbid, dark brown appearance during low flow periods to a light tan color with only slight turbidity during periods of high flow.

An oil scum was observed on the surface during low flow periods. A black deposit, presumably oil, was observed along the shoreline just above the water level throughout the basin.

Odors were variable in intensity but in most samples faint and predominantly gasoline. In some samples, faint oil, sewage, and solvent odors were apparent.

U.S. ARMY

U.S. LAKE SURVEY

DAILY MEAN WATER LEVELS

at BUFFALO, N.Y. For 1956 LAKE ERIE

Day	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
1	571 75	571 25	571 42	571 97	572 55	573 64	573 42	573 29	573 39	572 63	572 19	
2	1 94	1 48	1 82	572 12	2 62	3 36	3 47	572 74	3 47	2 93	2 22	
3	572 40	1 30	1 43	2 15	2 83	3 50	3 37	573 00	3 24	2 63	2 10	
4	2 36	1 27	1 35	2 87	2 81	3 48	572 65	3 10	3 28	2 76	2 06	
5	2 03	1 55	1 31	2 29	2 88	3 47	573 01	3 30	3 19	2 21	2 04	
6	571 67	1 08	1 23	2 07	2 65	3 40	3 28	3 28	3 46	2 77	2 17	
7	1 43	1 85	1 13	2 44	2 75	3 39	3 38	3 30	3 23	573 64	2 48	
8	1 69	1 31	574 83	2 35	2 61	3 42	3 42	3 43	3 22	3 52	2 84	
9	1 97	1 13	572 38	2 29	573 02	3 44	3 69	3 63	3 05	572 70	2 81	
10	1 84	1 33	571 33	2 23	3 06	3 47	3 67	3 73	3 27	2 54	2 08	
11	1 86	570 69	572 53	2 03	572 95	3 38	3 64	3 48	3 36	2 73	2 53	
12	1 78	572 05	571 78	2 28	573 22	3 54	3 42	3 44	3 10	2 46	2 81	
13	1 87	571 61	1 67	2 46	3 31	3 47	3 42	3 62	3 24	2 54	2 57	
14	1 91	1 29	1 69	2 36	3 73	3 43	3 70	3 58	3 34	2 47	2 20	
15	1 84	1 25	1 63	2 46	3 41	3 37	3 47	3 43	2 60	2 42	2 16	
16	1 73	570 90	1 00	2 88	3 85	3 29	3 33	3 51	2 89	2 41	574 16	
17	1 83	0 67	1 74	573 27	3 38	3 26	3 20	3 35	3 41	2 39	571 93	
18	1 69	571 58	1 20	572 89	3 49	572 80	3 25	3 49	3 17	2 03	1 91	
19	570 88	1 28	1 63	2 61	3 72	573 08	3 14	3 43	3 50	571 86	1 90	
20	571 58	1 49	1 91	2 58	3 34	3 37	3 20	3 30	3 20	572 40	1 99	
21	1 78	1 57	1 91	2 94	3 42	3 43	3 41	3 24	3 30	2 35	573 76	
22	1 91	1 54	572 04	2 57	3 51	3 36	3 40	3 66	2 81	2 28	3 63	
23	1 89	1 32	571 62	2 75	3 46	3 45	3 58	3 94	3 17	2 38	572 50	
24	1 64	1 11	1 86	2 49	3 45	3 58	3 54	3 37	3 05	571 35	2 19	
25	1 48	572 23	572 32	2 31	3 33	3 48	3 53	3 33	2 64	1 93	571 65	
26	1 55	571 67	2 07	2 41	3 37	3 32	3 24	3 38	2 33	572 26	1 95	
27	1 49	570 99	571 74	2 42	3 46	574 05	3 43	3 37	2 41	2 33	572 21	
28	1 30	571 49	1 30	2 45	3 32	573 70	3 34	3 37	2 66	571 96	2 94	
29	1 61	1 46	572 28	2 30	3 28	3 51	3 26	3 30	2 70	572 18	2 48	
30	1 44		2 58	2 77	3 61	3 43	3 30	3 20	3 04	2 21	2 16	
31	1 71		2 40		3 56		3 27	3 23		2 13		
Means	571 74	571 37	571 85	572 47	573 22	573 43	573 37	573 38	573 09	572 43	572 42	
Max.	572 60	574 17	577 45	575 72	575 13	574 80	574 80	575 04	575 25	574 48	578 44	
Day & Hr	1700 3	1925 25	1830 8	1635 7	1300 14	0500 27	1230 9	2125 23	2155 1	0340 7	1512 21	
Min.	570 27	569 55	569 53	571 21	571 94	572 14	572 06	572 33	571 82	570 97	571 10	
Day & Hr	0900 30	0716 17	2340 7	0100 8	0750 2	1245 18	0217 5	0500 2	1900 26	2343 24	1240 25	

Remarks ELEVATIONS ARE IN FEET AND REFER TO MEAN TIDE AT NEW YORK, 1935 DATUM. Annual Mean

AUTOMATIC GAGE FILE HDE 2-1

CORPS OF ENGINEERS
U.S. ARMY

MONTHLY AND ANNUAL FLOW
IN THOUSANDS OF CUBIC FEET PER SECOND OF THE
NIAGARA RIVER
AT
BUFFALO, NEW YORK

U.S. LAKE SURVEY
DETROIT MICH.

YEAR	JAN.	FEB.	MAR.	APR.	MAY	JUNE	JULY	AUG.	SEPT.	OCT.	NOV.	DEC.	MEAN
1940	163	159	165	178	188	198	198	191	191	184	187	183	182
1941	184	179	173	176	181	185	185	181	176	172	178	172	178
1942	162	162	171	189	197	201	205	202	198	192	195	196	189
1943	186	190	192	202	220	235	234	230	220	209	211	207	211
1944	189	185	188	202	216	221	217	208	203	196	192	194	201
1945	177	178	189	208	214	222	226	221	213	221	213	210	208
1946	204	194	196	206	207	219	221	214	203	197	198	196	205
1947	190	179	184	186	219	239	235	226	223	210	211	208	209
1948	195	190	203	220	230	230	229	219	208	198	199	194	210
1949	196	199	198	201	201	202	201	193	192	182	179	177	193
1950	191	196	196	209	216	213	208	203	198	194	196	203	202
1951	201	197	210	224	228	228	229	221	216	208	209	214	215
1952	220	227	231	243	242	242	241	231	228	219	210	212	229
1953	210	216	215	220	221	229	229	224	218	205	204	209	217
1954	194	191	205	217	224	223	221	215	210	214	217	216	212
1955	223	209	226	230	231	229	224	218	209	208	210	199	218
1956	186	178	188	200	215	218	218	218	212				

REVISED SEPT. 1956
ALL PREVIOUS DATA SUPERSEDED
DATA AFTER JULY 1956 ARE PROVISIONAL

FILE ICA-2-5

TABLE 2 -PHYSICAL AND CHEMICAL DATA

BUFFALO RIVER

Source	Date 1956	Description Color, odor, etc.	Dissolved Oxygen ppm	pH	Alkalinity ($CaCO_3$) ppm	Acidity ($CaCO_3$) ppm	Hardness ($CaCO_3$) ppm	Phenols ppb 4AA	Phenols ppb Gibbs	Cyanide ppb
Buffalo River										
Socony-Mobil Intake	1-23	Light gray Slightly turbid	8.0	7.5	140	10	215	243	234	<5
	2-15	Faint gasoline odor	9.8	7.2	70	4	120	9	11	<5
	6-19	Brown color Faint gasoline odor Turbid	2.2	7.2	110	10	190	-	146	<5
National Aniline Intake	1-18	Brown color, Slightly turbid Faint oil and sewage odor	8.0	6.7	72	30	216	857	1256	<5
	2-14	Grayish tan color Slightly turbid	11.0	7.3	80	6	135	92	79	<5
	2-16	Slight sewage odor	7.6	7.6	64	4	110	52	29	<5
	2-21	Light grayish tan color Moderately turbid Gasoline and sewage odor	9.0	7.5	66	6	125	70	73	<5
	3-13	Light grayish tan odor Moderately turbid	10.0	7.5	72	4	115	11	10	5
	3-21	Faint gasoline odor	10.8	7.2	86	12	155	-	-	-
	6-21	Dark brown color Faint solvent odor Turbid	0.4	6.8	72	30	250	-	-	-

TABLE 2 (Cont'd) - PHYSICAL AND CHEMICAL DATA

. BUFFALO RIVER

Source	Date 1956	Description Color, odor, etc.	Dissolved Oxygen ppm	pH	Alkalinity ($CaCO_3$) ppm	Acidity ($CaCO_3$) ppm	Hardness ($CaCO_3$) ppm	Phenols ppb 4AA	Phenols ppb Gibbs	Cyanide ppb
Buffalo River										
Donner-Hanna Intake	1-19	Greenish, gray- Turbid Oil & phenol odor	6.0	6.8	74	30	245	1118	773	<5
	1-20	Greenish-brown- Turbid Oil & sewage odor	4.8	6.8	60	36	265	935	903	<5
	2-13	Light grayish tan color Very little turbidity Faint oil and solvent odor	8.0	7.5	70	8	140	162	166	<5
	3-12	Grayish-tan color Moderately turbid Oil & gasoline odor	9.6	7.5	52	4	105	11	18	14
	6-19	Brown color Faint solvent and oil odor	1.4	7.0	114	8	220	-	288	88
	6-25	Brown color Turbid Faint oil & medicinal odor	1.6	7.4	90	12	180	595	-	44
	11-13	Dark brown color Slightly turbid Gasoline odor	1.4	6.8	72	116	300	-	-	-
	11-15	Brown color Slightly turbid Faint gasoline odor	0.9	7.2	90	14	320	-	-	-

TABLE 2 (Cont'd) - PHYSICAL AND CHEMICAL DATA

· BUFFALO RIVER

Source	Date 1956	Description Color, odor, etc.	Dissolved Oxygen ppm	pH	Alkalinity ($CaCO_3$) ppm	Acidity ($CaCO_3$) ppm	Hardness ($CaCO_3$) ppm	Phenols ppb 4AA	Phenols ppb Gibbs	Cyanide ppb
Buffalo River										
New York Central Bridge	6-20	Dark brown color Medicinal odor	0.0	7.1	96	28	225	-	136	<5
	6-22	Dark brown Very turbid Faint solvent & oil odor	0.4	6.9	90	22	200	-	170	<5
	11-8	Dark brown Slight turbidity Gasoline & medicinal odor	1.0	6.6	100	36	300	376	-	149
Michigan St. Bridge	1-16	Brownish color Some suspended material Slight oil odor	Temp. when collected 38° F. 8.4	6.8	80	20	198	812	936	<5
	1-19	Brownish color Turbid Slight oil odor	6.6	6.9	60	20	185	882	906	<5
	2-16	Grayish-tan color Slightly turbid Very faint sewage odor	8.6	7.3	62	8	120	264	255	<5
	3-15	Grayish-tan color Slightly turbid Faint gasoline odor	9.0	7.2	64	8	120	-	-	-

TABLE 2 (Cont'd) - PHYSICAL AND CHEMICAL DATA

BUFFALO RIVER

Source	Date 1956	Description Color, odor, etc.	Dissolved Oxygen ppm	pH	Alkalinity ($CaCO_3$) ppm	Acidity ($CaCO_3$) ppm	Hardness ($CaCO_3$) ppm	Phenols ppb 4AA	Phenols ppb Gibbs	Cyanide ppb
Buffalo River Michigan St. Bridge	6-20	Brown color Slight burnt rubber and oil odor	4.2	7.3	94	16	180	-	45	<5
	6-22	Light brown color Slightly turbid Very little odor	3.4	7.2	94	10	190	-	82	<5
	11-18	Light brown Slightly turbid Faint gasoline odor	1.8	6.8	92	-	225	123	-	80

Color, odor, and turbidity were generally less at Stations 1 and 5 than at the other stations.

The general appearance of the Buffalo River in the section sampled was in sharp contrast to observations made on tributaries upstream from the influence of the Buffalo basin industrial complex. The tributaries were clear, with no color, odor, or oil scum, and clean water forms of aquatic life were abundant.

During the January, February, and March sampling periods, dissolved oxygen values were near saturation at all stations and water temperatures were low (40° F). In June, water temperatures were much higher (85° F) and dissolved oxygen levels were quite low (0-2 ppm) at Stations 2, 3, and 4 but had increased to 4 ppm or higher at Station 5. During November, D.O. values were low at all of the stations at which samples were taken (3,4,5).

Most of the bio-assay test concentrations lost oxygen rapidly indicating a high oxygen demand. It was necessary to add oxygen during most of these tests to provide adequate oxygen for the test fish.

During all sampling periods, pH values were relatively uniform, ranging from 6.6 to 7.6. The higher values were obtained during high flow periods.

Other chemical characteristics such as alkalinity, acidity, and hardness were variable, depending primarily on river flows. Hardness values were much lower during high flow periods.

Phenols and cyanides were quite low during the February and March high flow periods. Phenols were highest (1.2 ppm) during January, when water

temperatures were low and flows also relatively low -- Cyanide values were highest (0.15 ppm) in November, but were also relatively high in June.

While the above comments apply to the comparatively few samples of Buffalo River water analyzed, it is realized that chemical conditions may fluctuate widely, depending on the release of numerous wastes under highly variable flow conditions. An effort is made only to point to certain characteristics which may affect aquatic life in receiving waters.

Toxicity to Fish

A summary of bio-assay results showing the direct toxicity of the Buffalo River waters to fish is shown in Table 3. The information on which these results are based, including concentrations tested, time for fish mortality, per cent of mortality, and bio-assay control data are shown in the Appendix.

Median tolerance limit (TL_m) values were obtained for 24, 48, and 96 hour periods. The 96 hour TL_m was used to compute the dilution ratio, which is the ratio of a unit volume of effluent to dilution water which produces a 50 per cent mortality of the test fish. This ratio times the Buffalo River flow gives the dilution volume or the total flow of receiving water required to reduce the toxicity to where a 50 per cent mortality of the test fish is produced. The following formula may be used for directly computing this dilution volume:

$$\frac{100 - TL_m}{TL_m} \times \text{Effluent Flow} = \text{Dilution Volume}$$

TABLE 3 - SUMMARY OF BIOASSAY DATA

BUFFALO RIVER

Source	Date 1956	Flow cfs	TLm (Median Tolerance Limit) (Per Cent Concentration) 24 Hr.	48 Hr.	96 Hr.	Dilution Volume cfs
Buffalo River						
Socony-Mobil Intake	1-23	119	100% Surv.	100% Surv.	100% Surv.(1)	-
	2-15	1510	100% Surv.	100% Surv.	100% Surv.	-
	6-19	68	100% Surv.	100% Surv.	100% Surv.	-
National Aniline Intake	1-18	93	100% Surv.	90% Surv.	70% Surv.	-
	2-14	717	100% Surv.	100% Surv.	100% Surv.	-
	2-16	1194	100% Surv.	100% Surv.	100% Surv.	-
	2-21	770	90% Surv.	90% Surv.	90% Surv.	-
	3-13	960	100% Surv.	100% Surv.	90% Surv.	-
	3-21	513	100% Surv.	100% Surv.	100% Surv.	-
	" (Shiners)	-	100% Surv.	100% Surv.	80% Surv.	-
	6-21	56	75	70	70	24
Donner-Hanna Intake	1-19	98	79	70	69	44
	1-20	91	60	51	51	88
	2-13	896	100% Surv.	100% Surv.	100% Surv.	
	3-12	1574	100% Surv.	100% Surv.	90% Surv.	
	6-19	68	29	29	29	167
	6-25	72	42	42	29	176
	11-13	80	51	51	51	77
	11-15	87	80% Surv.	60% Surv.	60% Surv.	-

(1) Per Cent Survival of Fish in Undiluted Sample.

TABLE 3 (Cont'd) - SUMMARY OF BIOASSAY DATA

BUFFALO RIVER

Source	Date 1956	Flow cfs	TLm (Median Tolerance Limit) (Per Cent Concentration) 24 Hr.	48 Hr.	96 Hr.	Dilution Volume cfs
Buffalo River						
New York Central Bridge	6-20	62	45	45	42	86
	6-22	56	37	37	29	137
	11-18	83	75	75	75	28
Michigan Street Bridge	1-16	204	100% Surv.	100% Surv.	80% Surv. (1)	-
	1-19	98	90% Surv.	70% Surv.	70% Surv.	-
	2-16	1194	100% Surv.	100% Surv.	90% Surv.	-
	3-15	690	100% Surv.	100% Surv.	100% Surv.	-
	6-20	62	80% Surv.	60% Surv.	60% Surv.	-
	6-22	56	80% Surv.	80% Surv.	60% Surv.	-
	11-8	83	100% Surv.	100% Surv.	100% Surv.	-

(1) Per Cent Survival of Fish in Undiluted Sample.

The dilution volumes represent conditions which would cause direct injury to fish upon short time exposure and are a direct comparative measure of toxicity. Liberal application factors must be applied to these results for complete protection of aquatic life.

The toxicity of the Buffalo River waters was highly variable depending on flow conditions as well as on sample locations. Toxicity values ranged from samples with no apparent toxicity to some samples during the June low flow period with ninety-six hour TL_m values of 29 per cent. The most highly toxic samples were immediately below major industrial waste sources (Stations 3 and 4).

During high flow periods in February and March, little or no toxicity was indicated at any of the sampling stations.

At the Socony-Mobil intake (Station 1) there was no mortality of the test fish in the undiluted river water samples even during the June low flow period. The toxicity increased downstream to the New York Central bridge (Station 4) but had dissipated to a large extent at Michigan Street bridge (Station 5). None of the samples taken at this point contained enough toxicity to establish a TL_m value, although there was some fish mortality in the undiluted samples.

It was not definitely established whether this decreased toxicity was entirely due to natural purification factors or may have been decreased partly by additional dilution from Lake Erie backwater. Two samples were taken farther upstream (Station 3) in November under approximately the same Buffalo River tributary flow conditions. One of these samples was taken when

lake levels were quite high and the toxicity had decreased considerably.

The bio-assay results reported were obtained under conditions in which oxygen was maintained at higher levels than sometimes are present in the Buffalo River. As many substances are more toxic at lower oxygen levels, more toxic conditions than are actually shown may at times exist.

While results are reported during a period of lowest flow for 1956, previous records show that much lower flows may sometimes occur. Under lower flow conditions, the concentration of wastes may be greater causing more toxic conditions than shown.

SIGNIFICANCE OF DATA

Characteristics which may Affect Aquatic Life

While Buffalo River waters during low flow periods were toxic to fish, the complexity of the situation and insufficient information made it impossible to determine the chemical components responsible for this toxicity.

It is realized that aquatic life protection is not required in the Buffalo River itself but certain characteristics of these waters may possibly have an effect on Lake Erie and the Niagara River, waters in which aquatic life protection is required.

This section of the report is primarily intended to provide information on the toxicity of some components of industrial wastes known to enter the Buffalo River and on those characteristics of Buffalo River waters which may affect aquatic life unless adequate dilution is available.

Bio-assays were conducted on some chemical compounds under similar experimental conditions to those of industrial effluent and river water samples. Following are 96 hour TL_m values obtained for these chemicals:

Chemical	96-hour TL_m ppm
Phenol	40
O-Cresol	24
Cyanide (CN)	0.24
Ammonia (N)	7.0
Sulfide (H_2S)	1.4
Benzene	56
Toluene	51
Xylene	28

The maximum values reported for phenol and cyanide (Table 2) would indicate that these components were not responsible for the toxicity in river water samples. Other phenolic compounds, however, have been reported toxic to fish in concentrations as low as 0.2 ppm.

Chemical information was not available on the amount of the other chemicals in river water samples. Previous information on similar samples indicate that these materials were not present in sufficient quantities to account for the toxicity.

There are, of course, many other chemical compounds which may be present in the Buffalo River, upon which no data on the quantity or toxicity were available.

During this study, pH values of the river samples were at levels which would not be expected to have any adverse effect on aquatic life; generally, pH values below 5 and above 9 may have a direct lethal effect. Within these limits, however, a change in pH may have an effect by increasing or decreasing the toxicity of various chemicals to fish. The toxicity of metals, cyanides, and sulfides may be increased by a decrease in pH while the toxicity of ammonia is greater at higher pH values.

Dissolved oxygen values were at levels which would definitely affect aquatic life (Table 2) in some of the low flow period samples. Oxygen depleting characteristics may have a definite effect on aquatic life unless adequate volumes of receiving water are available for dilution or assimilation. Low oxygen may also tend to increase the toxicity of certain chemicals (e.g. cyanide). For adequate protection of aquatic life, dissolved oxygen concentrations should be maintained at 5 ppm or above in waters receiving toxic materials.

Observations indicated fairly large quantities of oil in the Buffalo River. Oil may mix with other organic material, settle to the bottom in the form of a sludge, and have an adverse effect on bottom fish food organisms.

Small, sublethal quantities of oils, gasoline, phenols, and various solvents, especially benzene derivatives, are known to impart a taste to fish flesh.

High water temperatures may have an effect in increasing the toxicity

of some materials, reducing dissolved oxygen, and a direct effect on some organisms.

Color and turbidity apparently have no direct effect on fish. An indirect effect may be possible by a decrease in light penetration and consequently the productivity. Suspended materials may settle out and have an adverse effect on bottom food organisms and fish spawning.

Effect on Receiving Waters

Buffalo River waters, under low flow conditions, were toxic to fish. The dilution volumes necessary to reduce this toxicity to levels producing a 50 per cent mortality of the test fish (Table 3) would obviously not provide for complete protection of aquatic life. Liberal application factors must be used, which are based on the following major considerations:

(1) The bio-assay procedure measures 50 per cent mortality during a relatively short time period in non-renewed solutions. This must be related to no effect during continuous long time exposure.

(2) Test data apply directly to the species of fish used. While fathead minnows are of intermediate tolerance and compare favorably with many warm water "game" fishes, some locally important species of fish and fish food organisms may be more sensitive. Bio-assays conducted with a locally important forage fish, the emerald shiner (Notropis atherinoides), indicated this species was approximately twice as sensitive as fathead minnows.

(3) Toxicity may be variable. A few samples may give an indication of toxicity but maximum conditions may be missed. In many situations, maximum conditions of toxicity are the limiting factor as far as aquatic life is

concerned.

(4) Some conditions which may generally reduce but in some cases increase the magnitude of the application factor are the loss of volatiles, hydrolysis, oxidation, precipitation, and changes in water quality characteristics.

Based on the best available information an application factor of at least 3 would be necessary to prevent fish kills and as much as 10 for complete protection and propagation of fish.

The toxicity contributed by the industrial effluents on which bio-assays were conducted during this study is shown in Table 4. The maximum toxicity values found in the Buffalo River, a short distance below the effluent outfalls, during the various flow periods and seasons, are also shown.

It is obvious from this data that a considerable reduction in toxicity from that contributed by the individual industrial effluents takes place in the Buffalo River. The bio-assay data at Michigan Street bridge (Table 3) indicates a further reduction in toxicity near the river mouth. This apparent reduction in toxicity may be from such factors as mixing of effluents, loss of volatiles, hydrolysis, precipitation, oxidation, etc., but also may be from additional dilution by Lake Erie backwater. Only the tributary flows were used in computing dilution volumes.

It is apparent from these data that a fractional part of the Niagara River flow would provide adequate dilution to prevent toxicity to aquatic life. Based on the maximum toxicity figures for the Buffalo River in June and an application factor of ten, 1250 cfs would be needed. Even less would

TABLE 4 - COMPARATIVE TOXICITY OF EFFLUENTS DISCHARGED INTO THE BUFFALO RIVER

Source	Number Samples	Flow cfs	Median Tolerance Limit (TLm) Per Cent Concentration Range	Average	Dilution Volume cfs
Industrial Effluents					
A	3	20.6	37-42	40	32
B	7	17.4	4.4-16	9.1	174
C	7	10.5	13.5-28	20	42
D	8	2.8	4.0-24	9.6	26
E	14	9.85	2.9-22.5	11.0	80
TOTAL					354
Buffalo River	(Donner-Hanna Intake and New York Central Bridge)				
January	2	118	51-69	60	79
February-March	2	850	No Fish Mortality		-
June	4	59	29-42	32	125
November	2	83	51-75	62	51

be required if the further reduction in toxicity at Michigan Street bridge is considered.

While the toxicity from individual industrial effluents is substantially reduced in the basin, enough toxicity remains to present a threat to the Niagara River under abnormal conditions. Toxicity may build up in the Buffalo River during low flows and then may be rapidly released into Lake Erie and the Niagara River. (The toxicity in the Buffalo River may at times be much greater than this bio-assay study indicates. As previously discussed, tributary flows may be much lower than observed during this study. Industrial effluents are highly variable and a combination of circumstances may result in a considerably increased toxic load to the river on some occasions).

Additional dilution water in the Buffalo River during low flow periods should minimize this possibility.

The low dissolved oxygen content and oxygen depleting characteristics of Buffalo River waters may have an effect in a border area where the Buffalo River enters Lake Erie but would not be expected to affect the Niagara River significantly.

The presence of oils that form bottom sludges as well as large amounts of suspended materials may enter Lake Erie and the Niagara River where they may settle out and have an effect on bottom fish food organisms and fish spawning.

The possibility also exists that an off-flavor in fish flesh may be produced by small quantities of oil, gasoline, phenol, and solvents.

A study of the aquatic biota in these areas could readily determine the

extent of damage, if any, from the above causes.

CONCLUSIONS

Bio-assays have shown that Buffalo River waters are toxic to fish during low flow periods but are relatively non-toxic during periods of moderate to high flow. The toxicity contributed to the basin by industrial effluents is substantially reduced before entry into Lake Erie. Under normal flow conditions, little or no effect from toxicity would be expected in the Niagara River.

The buildup of toxicity in the Buffalo River basin during low flows, with the possibility of a rapid release into receiving waters does present some threat to aquatic life. As long as Buffalo River waters remain toxic, there is the possibility of a sudden flush out with some destruction of fish in portions of Lake Erie and the Niagara River. Additional dilution water in the Buffalo River during low flow periods should minimize this possibility.

However, with the large quantities of unknown toxic materials now entering the Buffalo River basin, the threat to aquatic life cannot be completely eliminated. Bio-assays could be used by industries to help locate sources of major toxic wastes with the aim of reducing or eliminating highly toxic materials.

Biological field studies could be made to determine the extent of damage, if any, to aquatic life in Lake Erie and the Niagara River from oxygen depletion, oil sludges, and suspended solids.

APPENDIX TABLE A1 -BIOASSAY DATA

BUFFALO RIVER WATER

TEST FISH - FATHEAD MINNOWS
DILUTION WATER - LAKE ERIE

SOURCE AND METHOD OF COLLECTION OF SAMPLE	DATE OF COLLECTION	CONCENTRATION TESTED PERCENT	NUMBER OF TEST FISH	VOLUME OF TEST SAMPLE LITERS	TIME OF DEATH			PERCENT SURVIVAL				CHEMICAL AND PHYSICAL DATA							REMARKS
					FIRST FISH	HALF OF FISH	ALL OF FISH	24 HOURS	48 HOURS	72 HOURS	96 HOURS	TIME	TEMP. °C	DISSOLVED OXYGEN ppm.	p H	TOTAL ALK ($CaCO_3$) ppm.	TOTAL ACIDITY ($CaCO_3$) ppm	VERSENATE HARDNESS ppm.	
Secony Mobil Intake	1-23-56	100	10	20				100	100	100	100	Initial	23	8.0	7.5	140	10	215	Light gray
												96 hrs.	23	4.6	7.8	148	4	230	Faint gasoline odor
8-Hr.Composite		75	10	20				100	100	100	100	Initial		8.0	7.6	128	6	190	Slightly turbid
7 AM - 3 PM												96 hrs.		4.6	7.9	134	6	210	
Fish Added		56	10	20				100	100	100	100	Initial		8.0	7.7	118	4	165	
12:00 N 1-24												96 hrs.		4.8	7.9	130	4	180	
		Control	10	20				100	100	100	100	Initial		7.6	8.0	98	2	125	
												96 hrs.		4.4	7.8	106	4	145	
		No Tlm Value - 100% survival of fish																	
Secony Mobil Intake	2-15-56	100	10	20				100	100	100	100	Initial	25	9.8	7.2	70	4	120	Light gray
												96 hrs.	25	4.8	7.6	72	4	120	Faint gasoline odor
8-Hr.Composite		56	10	20				100	100	100	100	Initial		8.4	7.5	82	2	120	Slightly turbid
7:00 AM 3:00 PM												96 hrs.		4.8	7.7	84	4	120	
Fish Added		Control	10	20				100	100	100	100	Initial		7.6	8.1	96	1	125	
11:00 AM 2-16												96 hrs.		4.0	7.7	100	6	130	
		No Tlm Value - 100% survival of fish																	
Secony Mobil Intake	6-19-56	100	5	10				100	100	100	100	Initial	23	2.2	7.2	110	10	190	Brown
												96 hrs.	23	4.2	7.7	110	6	210	Faint gasoline odor
8-Hr.Composite		56	10	20				100	100	100	100	Initial		4.8	7.4	100	8	160	24-Hr.DO - 2.4
7 AM - 3 PM												96 hrs.		5.0	7.8	102	4	155	48 Hr.DO - 4.4
Fish Added		32	10	20				100	100	100	100	Initial		6.4	7.7	92	6	155	
5:00 PM 6-19												96 hrs.		4.2	7.8	100	4	150	
		Control	10	20				100	100	100	100	Initial		7.8	8.2	90	0	130	
												96 hrs.		5.8	7.9	94	2	130	
		No Tlm Value - 100% survival of fish																	
Oxygenated		100	5	10				100	100	100	100	Initial		Same as above					48 Hr.DO - 18.6
												96 hrs.		6.4	7.7				

APPENDIX TABLE A2 -BIOASSAY DATA

TEST FISH - FATHEAD MINNOWS
DILUTION WATER - LAKE ERIE

BUFFALO RIVER WATER

SOURCE AND METHOD OF COLLECTION OF SAMPLE	DATE OF COLLECTION	CONCENTRATION TESTED PERCENT	NUMBER OF TEST FISH	VOLUME OF TEST SAMPLE LITERS	TIME OF DEATH			PERCENT SURVIVAL				CHEMICAL AND PHYSICAL DATA							REMARKS
					FIRST FISH	HALF OF FISH	ALL OF FISH	24 HOURS	48 HOURS	72 HOURS	96 HOURS	TIME	TEMP. °C	DISSOLVED OXYGEN ppm.	p H	TOTAL ALK ($CaCO_3$) ppm.	TOTAL ACIDITY ($CaCO_3$) ppm	VERSENATE HARDNESS ppm.	
National Aniline Intake	1-18-56	100	10	20	40 hrs.	-	-	100	90	90	70	Initial	20	8.0	6.7	72	30	216	Brown.
												96 hrs.	23	5.4	7.3	68	4	225	Faint oil and sewage odor.
8-Hr.Composite																			
In Lab		56	5	10	-	-	-	100	100	100	80	Initial	23	7.8	6.9	80	16	186	Slight turbidity.
2:00 PM 1-18												96 hrs.	23	6.2	7.6	80	4	180	
Fish Added		Control	10	20	-	-	-	100	100	100	100	Initial		7.3	8.0	96	2	128	
5:30 PM 1-18												96 hrs.		6.8	7.8	100	4	130	
		No Tlm Value - 70% survival in 96 hrs.																	
National Aniline Intake	2-14-56	100	10	20	-	-	-	100	100	100	100	Initial	18	11.0	7.3	80	6	135	Light greyish tan.
												96 Hrs.	25	4.0	7.6	80	6	135	Faint sewage odor.
8-Hr.Composite																			Slight turbidity.
In Lab		56	10	20	-	-	-	100	100	100	100	Initial	23	9.2	7.5	92	4	135	
10:00 AM 2-14												96 Hrs.	25	5.0	7.7	90	6	130	
Fish Added		Control	10	20	-	-	-	100	100	100	100	Initial	25	7.6	8.1	98	1	125	
5:00 PM 2-14												96 Hrs.	25	4.6	7.8	100	4	130	
		No Tlm Value - 100% survival in 96 hrs.																	
National Aniline Intake	2-16-56	100	10	20	-	-	-	100	100	100	100	Initial	25	7.6	7.6	64	4	110	Light greyish tan.
												96 Hrs.	25	2.6	7.6	70	6	115	Faint sewage odor.
8-Hr.Composite																			Slight turbidity.
In Lab																			
2:00 PM 2-16																			
Fish Added																			
3:00 PM 2-19																			
		No Tlm Value - 100% survival in 96 hrs.																	
National Aniline Intake	2-21-56	100	10	20	6-24 hrs.	-	-	90	90	90	90	Initial	25	9.0	7.5	66	6	125	Light greyish tan.
												96 hrs.		4.6	7.2	64	6	125	Gasoline and sewage odor.
8-Hr.Composite								100	100	100	100	Initial		8.4	7.7	80	6	125	Slight turbidity.
In Lab		56	10	20								96 hrs.		5.4	7.5	84	4	125	
11:30 AM 2-21								100	100	100	100	Initial		8.4	8.1	100	1	130	
Fish Added		Control	10	20								96 hrs.		5.0	7.6	102	4	130	
9:00 AM 2-22																			
		No Tlm Value - 90% survival in 96 hrs.																	
National Aniline Intake	3-13-56	100	10	20	80 hrs.	-	-	100	100	100	90	Initial	24	10.0	7.5	72	4	115	Light greyish tan.
												96 hrs.		5.0	7.4	72	6	110	Faint gasoline odor.
8-Hr.Composite																			Slight turbidity.
In Lab		56	5	10				100	100	100	100	Initial		9.0	7.7	80	2	115	
2:00 PM 3-13												96 hrs.		5.8	7.6	82	6	120	
Fish Added		Control	10	20				100	100	100	100	Initial		8.0	8.1	90	1	125	
9:00 AM 3-14												96 hrs.		5.4	8.0	94	4	125	
		No Tlm Value - 90% survival in 96 hrs.																	

APPENDIX TABLE A3 -BIOASSAY DATA

BUFFALO RIVER WATER

TEST FISH - FATHEAD MINNOWS AND SHINERS
DILUTION WATER - LAKE ERIE

SOURCE AND METHOD OF COLLECTION OF SAMPLE	DATE OF COLLECTION	CONCENTRATION TESTED PERCENT	NUMBER OF TEST FISH	VOLUME OF TEST SAMPLE LITERS	TIME OF DEATH			PERCENT SURVIVAL				CHEMICAL AND PHYSICAL DATA							REMARKS
					FIRST FISH	HALF OF FISH	ALL OF FISH	24 HOURS	48 HOURS	72 HOURS	96 HOURS	TIME	TEMP. °C	DISSOLVED OXYGEN ppm.	p H	TOTAL ALK ($CaCO_3$) ppm.	TOTAL ACIDITY ($CaCO_3$) ppm.	VERSENATE HARDNESS ppm.	
National Aniline Intake	3-21-56	100	5	10	-	-	-	100	100	100	100	Initial	23	10.8	7.2	86	12	155	Grayish tan Faint gasoline odor Slight turbidity
8-Hr.Composite												96 hrs.		5.2	7.4	90	6	155	
In Lab		56	5	10	-	-	-	100	100	100	100	Initial		9.4	7.5	88	6	140	
10:00 AM												96 hrs.		5.6	7.5	92	8	135	
Fish Added		Control	5	10	-	-	-	100	100	100	100	Initial		9.0	8.1	90	2	120	
7:30 PM 3-21												96 hrs.		5.8	7.3	92	6	120	
		No TLm Value		100% Survival in 96 hrs.															
National Aniline Intake	3-21-56	100	5	10	72 hrs	-	-	100	100	80	80	Initial	23	9.6	7.1	88	10	160	Same as above
Same as above												96 hrs.		4.4	7.6	96	6	155	
Shiners		56	5	10				100	100	100	100	Initial		9.0	7.4	90	6	150	
(Notropis												96 hrs.		4.8	7.7	98	4	130	
atherinoides		32	5	10				100	100	100	100	Initial		9.0	7.7	90	4	135	
Fish Added												96 hrs.		5.0	7.7	104	4	130	
10:00 AM 3-22		Control	5	10				100	100	100	100	Initial		9.0	8.1	90	2	120	
												96 hrs.		6.2	7.6	96	4	120	
		No TL m Value		80% Survival in 96 hrs.															
National Aniline Intake	6-21-56	100	5	10	2 hrs	4 hrs.	4 hrs.	0	0	0	0	Initial	23	0.4	6.8	72	30	250	Dark Brown Paint solvent odor Low D.O.
8-Hr.Composite												4 hrs.		0.0	6.5	62	35	205	
In Lab		56	5	10	29-46 hrs			100	80	80	80	Initial		4.4	6.8	76	12	200	
7-3 PM 6-21												96 hrs		4.6	7.3	78	6	185	
Fish Added		32	5	10	29-46 hrs			100	80	80	80	Initial		6.0	7.1	80	9	170	
11:00 AM 6-22												96 hrs.		5.4	7.7	84	4	160	
		Control	10	20	96 hrs			100	100	100	90	Initial		7.8	8.2	94	0	135	
												96 hrs.		4.8	7.7	96	4	130	
		TLm (Median Tolerance Limit) - Per cent Concentration						75	70	70	70								
Same as above	6-21-56	100	5	10	3 hrs	4 hrs	29-46 hrs	20	0	0	0	Initial	23	4.4	-	-	-	-	
Oxygenated												48 hrs.		5.6	7.4	94	8	225	Same as above. No reduction in toxicity when oxygenated.
		56	5	10	7-22 hrs			80	80	80	80	Initial		-	-	-	-	-	
												96 hrs.		7.6	7.8	80	4	175	
		32	5	10	7-22 hrs			80	80	80	80	Initial		-	-	-	-	-	
												96 hrs.		7.0	7.9	84	4	160	

APPENDIX TABLE A4 -BIOASSAY DATA

BUFFALO RIVER WATER

TEST FISH - FATHEAD MINNOWS
DILUTION WATER - LAKE ERIE

SOURCE AND METHOD OF COLLECTION OF SAMPLE	DATE OF COLLECTION	CONCENTRATION TESTED PERCENT	NUMBER OF TEST FISH	VOLUME OF TEST SAMPLE LITERS	TIME OF DEATH			PERCENT SURVIVAL				CHEMICAL AND PHYSICAL DATA							REMARKS
					FIRST FISH	HALF OF FISH	ALL OF FISH	24 HOURS	48 HOURS	72 HOURS	96 HOURS	TIME	TEMP. °C	DISSOLVED OXYGEN ppm.	p H	TOTAL ALK ($CaCO_3$) ppm.	TOTAL ACIDITY ($CaCO_3$) ppm	VERSENATE HARDNESS ppm.	
Donner-Hanna Intake	1-19-56	100	10	20	9-22 hrs	9-22 hrs	9-22 hrs	0	0	0	0	Initial	23	6.0	6.8	74	30	245	Greenish gray
8-Hr.Composite												22 hrs.	23	3.0	7.0	66	20	250	Oil and phenol odor
In Lab		75	5	10	5-22 hrs	26-44 hrs	-	60	40	40	40	Initial		5.8	7.0	72	14	215	Turbid
5:00 PM 1-19												96 hrs.		4.6	7.4	74	8	215	
Fish Added		56	10	20	30-46 hrs	-	-	100	80	70	70	Initial		6.4	7.0	80	16	220	
11:30 AM 1-20												96 hrs.		4.2	7.5	82	6	195	
		Control	10	20	-	-	-	100	100	100	100	Initial		7.6	8.2	94	1	122	
												96 hrs.		5.6	7.7	100	2	125	
		TLm (Median Tolerance Limit) - Per cent Concentration						79	70	69	69								
Donner-Hanna Intake	1-20-56	100	10	20	1-16 hrs.	1-16 hrs	1-16 hrs.	0	0	0	0	Initial	23	4.8	6.8	60	36	265	Greenish brown
8-Hr.Composite												16 hrs.	23	0.2	6.6	54	24	265	Oil and sewage odor
In Lab		75	5	10	4-22 hrs	4-32 hrs	29-46 hrs	20	0	0	0	Initial		5.0	6.8	62	16	235	Turbid
3:00 PM 1-20												46 hrs.		2.6	7.0	68	8	220	Low D.O.
Fish Added		56	10	20	1-16 hrs	24-38 hrs	-	60	40	40	40	Initial		5.8	7.0	72	22	205	
5:00 PM 1-21												96 hrs.		4.8	7.4	74	6	205	
		32	10	20	-	-	-	100	100	100	100	Initial		6.8	7.4	84	4	165	
												96 hrs.		5.0	7.8	94	4	200	
		Control	10	20				100	100	100	100	Initial		7.8	8.1	100	2	130	
												96 hrs.		5.0	7.6	100	6	125	
		TLm (Median Tolerance Limit) - Per cent Concentration						60	51	51	51								
Donner-Hanna Intake	2-13-56	100	10	20	-	-	-	100	100	100	100	Initial	25	8.0	7.5	70	8	140	Light grayish tan
8-hr.Composite												96 hrs.	25	3.4	7.5	66	6	130	Faint oil and solvent odor
In Lab		56	10	20	-	-	-	100	100	100	100	Initial		8.0	7.6	86	4	140	Slight turbidity
4:00 PM 2-13												96 hrs.		4.0	7.6	84	6	125	
Fish Added		Control	10	20	-	-	-	100	100	100	100	Initial		7.6	8.2	96	1	135	
12 Noon 2-14												96 hrs.		4.6	7.8	100	6	125	
		No TLm Value - 100% survival in 96 hrs.																	
Donner-Hanna Intake	3-12-56	100	10	20	79-94 hr.	-	-	100	100	100	90	Initial	23	9.6	7.5	52	4	105	Grayish tan
8-hr.Composite												96 hrs.	24	6.0	7.3	56	4	110	Oil and gasoline odor
In Lab		56	10	20	-	-	-	100	100	100	100	Initial		8.4	7.8	74	4	115	Slight turbidity
5:00 PM 3-12												96 hrs.		6.0	7.5	74	4	120	
Fish Added		Control	10	20	-	-	-	100	100	100	100	Initial		7.8	8.1	94	0	125	
11:00 AM 3-13												96 hrs.		5.4	8.0	94	4	125	
		No TLm Value - 90% survival in 96 hrs.																	

APPENDIX TABLE A5 -BIOASSAY DATA

BUFFALO RIVER WATER

TEST FISH - FATHEAD MINNOWS
DILUTION WATER - LAKE ERIE

SOURCE AND METHOD OF COLLECTION OF SAMPLE	DATE OF COLLECTION	CONCENTRATION TESTED PERCENT	NUMBER OF TEST FISH	VOLUME OF TEST SAMPLE LITERS	TIME OF DEATH			PERCENT SURVIVAL				CHEMICAL AND PHYSICAL DATA							REMARKS
					FIRST FISH	HALF OF FISH	ALL OF FISH	24 HOURS	48 HOURS	72 HOURS	96 HOURS	TIME	TEMP. °C	DISSOLVED OXYGEN ppm.	p H	TOTAL ALK ($CaCO_3$) ppm.	TOTAL ACIDITY ($CaCO_3$) ppm	VERSENATE HARDNESS ppm.	
Donner-Hanna Intake	6-19-56	100	5	10	1 hr.	1½ hrs.	2 hrs.	0	0	0	0	Initial	23	1.4	7.0	114	8	220	Brown Faint solvent and oil odor Turbid Low D.O.
8-hr.Composite												2 hrs.		1.0	7.1	104	30	208	
In Lab		56	5	10	1 hr.	4 hrs.	6 hrs.	0	0	0	0	Initial		4.8	6.9	92	8	200	
4 PM - 6-19												6 hrs.		3.2	7.4	96	12	180	
Fish Added		32	5	10	8 hrs.	9 hrs.	-	40	40	40	40	Initial	23	5.0	7.3	92	8	165	
11:30 AM 6-20												96 hrs.	23	5.8	7.8	92	4	155	
		18	5	10				100	100	100	100	Initial		6.4	7.8	92	4	140	
												96 hrs.		5.6	7.9	96	2	145	
		Control	10	20	96 hrs.	-	-	100	100	100	90	Initial		7.8	8.2	90	0	130	
												96 hrs.		5.8	7.9	94	2	130	
		TLm (Median Tolerance Limit) - Per cent Concentration						29	23	23	23								
Same as above	6-19-56	100	5	10	2 hrs.	4 hrs.	6 hrs.	0	0	0	0	Initial	23	4.0	-	-	-	-	Slight decrease in toxicity when oxygen maintained.
Oxygenated												6 hrs.		13.0	7.2	98	22	225	
Fish Added		56	5	10	4 hrs.	5 hrs.	9-22 hrs.	0	0	0	0	Initial		-	-	-	-	-	
1:00 PM 6-20												22 hrs.		12.4	7.4	94	6	165	
		32	5	10	38-46 hrs.			100	60	60	60	Initial		-	-	-	-	-	
												96 hrs.		6.6	7.8	94	4	155	
Donner-Hanna Intake	6-25-56	100	5	10	1 hr.	3 hrs.	3 hrs.	0	0	0	0	Initial	23	1.6	7.4	90	12	180	Brown Faint oil and medicinal odor Turbid
8-hr.Composite												3 hrs.		4.0	7.1	82	16	225	
In Lab		56	5	10	5-17 hrs.	25-41 hrs	-	60	40	40	40	Initial	23	4.6	7.5	92	8	175	
4:00 PM 6-25												96 hrs.	23	2.8	7.9	-	-	-	
Fish Added		32	5	10	5-17 hrs.	96 hrs.	-	80	60	60	40	Initial		6.0	7.6	94	6	155	
3:00 PM 6-26												96 hrs.		2.2	7.5	-	-	-	
		Control	10	20	-	-	-	100	100	100	100	Initial		8.2	8.2	94	0	130	
												96 hrs.		3.0	7.7	-	-	-	
		TLm (Median Tolerance Limit) - Per cent Concentration						52	42	42	29								
Donner-Hanna Intake	11-13-56	100	5	10	2 hrs.	2 hrs.	3 hrs.	0	0	0	0	Initial		1.4	6.8	72	16	300	Dark brown Gasoline odor Slight turbidity Possible low D.O.
8-hr.Composite												3 hrs.		3.2	7.1	-	-	-	
In Lab		56	5	10	5-21 hrs	5-21 hrs	-	40	40	40	40	Initial	24	3.6	7.1	86	14	240	
5:00 PM 11-13												96 hrs.	24	7.6	7.8	-	-	-	
Fish Added		32	5	10	-	-	-	100	100	100	100	Initial		4.8	7.3	90	8	190	
12:30 PM 11-15												96 hrs.		5.0	7.8	-	-	-	
		TLm (Median Tolerance Limit) - Per cent Concentration						51	51	51	51								
Donner-Hanna Intake	11-15-56	100	5	10	2-18 hrs	-	-	80	60	60	60	Initial	24	0.9	7.2	90	14	320	Brown Faint gasoline odor Slight turbidity Low D.O.
8-hr.Composite												96 hrs.	24	7.0	7.9	-	-	-	
In Lab 5 PM 11-15		56	5	10	-	-	-	100	100	100	100	Initial		4.2	7.3	96	10	250	
Fish Added 3:15 PM 11-16												96 hrs.		4.8	7.7				
		No TLm value - 60% survival in 96 hrs.																	

APPENDIX TABLE A6 -BIOASSAY DATA

BUFFALO RIVER WATER

TEST FISH - FATHEAD MINNOWS
DILUTION WATER - LAKE ERIE

SOURCE AND METHOD OF COLLECTION OF SAMPLE	DATE OF COLLECTION	CONCENTRATION TESTED PERCENT	NUMBER OF TEST FISH	VOLUME OF TEST SAMPLE LITERS	TIME OF DEATH			PERCENT SURVIVAL				CHEMICAL AND PHYSICAL DATA							REMARKS
					FIRST FISH	HALF OF FISH	ALL OF FISH	24 HOURS	48 HOURS	72 HOURS	96 HOURS	TIME	TEMP. °C	DISSOLVED OXYGEN ppm.	p H	TOTAL ALK ($CaCO_3$) ppm.	TOTAL ACIDITY ($CaCO_3$) ppm	VERSENATE HARDNESS ppm.	
Buffalo River	6-20-56	100	5	10	1 hr	2 hrs	2 hrs	0	0	0	0	Initial	23	0.0	7.1	96	28	275	Dark Brown. Medicinal Odor.
New York Central												2 hrs.		0.4	7.0	94	22	205	Low D.O.
Bridge		56	5	10	3-15 hrs	3-15 hrs	-	20	20	20	20	Initial		4.0	7.3	92	18	175	
4-hr. Composite												96 hrs.		5.4	7.8	100	4	190	
In Lab		32	5	10	63 hrs	-	-	100	100	80	80	Initial		5.8	7.5	90	8	150	
1:00 PM 6-20												96 hrs.		5.2	7.8	96	4	150	
Fish Added		Control	10	20	96 hrs.	-	-	100	100	100	90	Initial		7.8	8.2	90	0	130	
6:00 PM 6-20												96 hrs.		5.8	7.9	94	2	130	
		TL_m (Median Tolerance Limit) - Per cent Concentration						45	45	42	42								
Same as above	6-20-56	100	5	10	3-15 hrs	3-15 hrs	-	20	20	20	20	Initial		4.0	-	-	-	-	Slight reduction in toxicity when oxygen added
Oxygenated												96 hrs.		6.4	7.7	102	6	205	
Fish Added		56	5	10	3-15 hrs	19 hrs	-	40	40	40	40	Initial		-	-	-	-	-	
6:00 PM 6-20												96 hrs.		7.6	7.8	100	4	180	
		32	5	10	-	-	-	100	100	100	100	Initial		-	-	-	-	-	
												96 hrs.		5.0	7.7	96	4	155	
Buffalo River	6-22-56	100	5	10	1 hr.	1 hr.	1 hr.	0	0	0	0	Initial	23	0.4	6.9	90	22	200	Dark brown Paint solvent and oil odor
New York Central Bridge												1 hr.		0.6	6.9	88	22	200	
		56	5	10	1-17 hrs	1-17 hrs	-	20	20	20	20	Initial		4.4	7.2	92	8	180	Very turbid Low D.O.
4-hr. Composite												96 hrs.		5.8	7.7	94	4	185	
In Lab 1 PM 6-22		32	5	10	1-17 hrs	72-88 hrs	-	60	60	60	40	Initial		8.2	7.4	92	6	165	
Fish Added												96 hrs.		5.4	7.8	94	4	150	
4:00 PM 6-22		Control	10	20	96 hrs.	-	-	100	100	100	90	Initial		7.8	8.2	92	0	135	
												96 hrs.		4.8	7.7	96	4	130	
		TL_m (Median Tolerance Limit) - Per cent Concentration						37	37	37	28								
Same as above	6-22-56	100	5	10	1-17 hrs	1-17 hrs	-	40	20	20	20	Initial		9.6	-	-	-	-	Slight reduction in toxicity when oxygen added
Oxygenated												96 hrs.		6.4	7.8	90	4	225	
Fish Added		56	5	10	1-17 hrs	-	-	60	40	40	40	Initial		-	-	-	-	-	
4:00 PM 6-22												96 hrs.		6.4	7.8	94	4	185	
		32	5	10	-	-	-	80	80	80	60	Initial			-	-	-	-	
												96 hrs.		5.4	7.8	94	4	150	
Buffalo River	11-8-56	100	5	10	7 hrs.	8 hrs.	8-24 hrs.	0	0	0	0	Initial	21	1.0	6.6	100	36	300	Dark brown Gasoline and medicinal odor
New York Central Bridge												24 hrs.	21	10.8	7.7	-	-	-	
		56	5	10	-	-	-	100	100	100	100	Initial	23	4.9	7.1	92	-	215	Slight turbidity
4 hr. Composite												96 hrs.	23	4.0	7.6	-	-	-	
In Lab 12 N 11-8		32	5	10	-	-	-	100	100	100	100	Initial		6.0	7.4	100	-	190	
Fish Added 10 AM 11-9												96 hrs.		-	-	-	-	-	
		TL_m (Median Tolerance Limit) - Per cent Concentration						75	75	75	75								

APPENDIX TABLE A7 -BIOASSAY DATA

BUFFALO RIVER WATER

TEST FISH - FATHEAD MINNOWS
DILUTION WATER - LAKE ERIE

SOURCE AND METHOD OF COLLECTION OF SAMPLE	DATE OF COLLECTION	CONCENTRATION TESTED PERCENT	NUMBER OF TEST FISH	VOLUME OF TEST SAMPLE LITERS	TIME OF DEATH			PERCENT SURVIVAL				CHEMICAL AND PHYSICAL DATA							REMARKS
					FIRST FISH	HALF OF FISH	ALL OF FISH	24 HOURS	48 HOURS	72 HOURS	96 HOURS	TIME	TEMP. °C	DISSOLVED OXYGEN ppm.	p H	TOTAL ALK ($CaCO_3$) ppm.	TOTAL ACIDITY ($CaCO_3$) ppm	VERSENATE HARDNESS ppm.	
Buffalo River	1-16-56	100	10	20	68-84 hrs	-	-	100	100	100	80	Initial	17	8.4	6.8	80	20	198	Brown
Michigan St.												96 hrs.	23	4.8	7.3	80	6	215	Faint oil odor
bridge		75	5	10	84-96 hrs	-	-	100	100	100	80	Initial	19	8.0	6.9	84	14	182	Slight turbidity
4-Hr.Composite												96 hrs.	23	5.4	7.5	84	4	190	
In Lab		56	10	20	-	-	-	100	100	100	100	Initial	20	7.8	7.1	86	10	172	
1:25 PM 1-16												96 hrs.	23	5.2	7.6	86	4	175	
Fish Added		Control	10	20	-	-	-	100	100	100	100	Initial	23	7.8	8.2	100	0	132	
10:00 PM 1-16												96 hrs.	23	6.0	7.8	100	3	130	
		No Tlm value. 80% survival in 96 hrs.																	
Buffalo River	1-19-56	100	10	20	23 hrs.	-	-	90	70	70	70	Initial	22	6.6	6.9	60	20	185	Brown
Michigan St.												96 hrs.	23	4.8	7.3	62	6	180	Faint oil odor
bridge		75	5	10	-	-	-	100	100	100	100	Initial	22	6.8	7.0	70	14	165	Turbid
4-Hr.Composite												96 hrs.	23	5.2	7.4	72	6	170	
In Lab		56	10	20	-	-	-	100	100	100	100	Initial	22	6.8	7.1	76	10	155	
1:20 PM 1-19												96 hrs.	23	5.8	7.5	80	6	155	
Fish Added		Control	10	20	-	-	-	100	100	100	100	Initial	22	7.6	8.2	94	1	122	
11:30 AM 1-20												96 hrs.	23	5.6	7.7	100	2	125	
		No Tlm value. 70% survival in 96 hrs.																	
Buffalo River	2-16-56	100	10	20	54 hrs.	-	-	100	100	90	90	Initial	24	8.6	7.3	62	8	120	Greyish tan
Michigan St.												96 hrs.	25	4.6	7.5	66	10	130	Faint sewage odor
bridge		56	10	20	-	-	-	100	100	100	100	Initial		8.4	7.5	80	4	120	Slight turbidity
4-Hr.Composite												96 hrs.		5.0	7.6	82	6	130	
In Lab		Control	10	20	-	-	-	100	100	100	100	Initial		7.6	8.1	100	2	125	
1:30 PM 2-16												96 hrs.		4.8	7.5	100	4	130	
Fish Added																			
12:00 Noon 2-17																			
		No Tlm value. 90% survival in 96 hrs.																	
Buffalo River	3-15-56	100	10	20	-	-	-	100	100	100	100	Initial	23	9.0	7.2	64	8	120	Greyish tan
Michigan St.												96 hrs.	23	4.8	7.4	66	4	125	Faint gasoline odor
bridge		56	10	20	-	-	-	100	100	100	100	Initial		8.6	7.5	76	6	120	Slight turbidity
4-Hr.Composite												96 hrs.		5.6	7.5	74	4	120	
In Lab		Control	10	20	-	-	-	100	100	100	100	Initial		8.4	8.0	90	2	115	
1:30 PM 3-15												96 hrs.		5.8	7.8	92	6	115	
Fish Added																			
9:00 AM 3-16																			
		No Tlm value. 100% survival in 96 hrs.																	

APPENDIX TABLE 46 -BIOASSAY DATA

BUFFALO RIVER WATER

TEST FISH - FATHEAD MINNOWS
DILUTION WATER - LAKE ERIE

SOURCE AND METHOD OF COLLECTION OF SAMPLE	DATE OF COLLECTION	CONCENTRATION TESTED PERCENT	NUMBER OF TEST FISH	VOLUME OF TEST SAMPLE LITERS	TIME OF DEATH			PERCENT SURVIVAL				CHEMICAL AND PHYSICAL DATA							REMARKS
					FIRST FISH	HALF OF FISH	ALL OF FISH	24 HOURS	48 HOURS	72 HOURS	96 HOURS	TIME	TEMP. °C	DISSOLVED OXYGEN ppm.	p H	TOTAL ALK ($CaCO_3$) ppm.	TOTAL ACIDITY ($CaCO_3$) ppm	VERSENATE HARDNESS ppm.	
Buffalo River	6-20-56	100	5	10	3-15 hrs	-	-	80	60	60	60	Initial	23	4.2	7.3	94	16	180	Brown
Michigan St.												96 hrs.	23	5.4	7.7	106	4	175	Faint burnt rubber and oil odor
bridge		56	5	10	24-38 hrs	-	-	100	60	60	60	Initial		6.0	7.5	90	10	150	Slight turbidity
4-Hr.Composite												96 hrs.		5.8	7.8	98	4	155	
In Lab		32	5	10	-	-	-	100	100	100	100	Initial		6.8	7.7	90	4	145	
1:00 PM 6-20												96 hrs.		6.2	7.8	96	4	145	
Fish Added		Control	10	20	-	-	-	100	100	100	90	Initial		7.8	8.2	90	0	130	
6:00 PM 6-20												96 hrs.		5.8	7.9	94	2	130	
		No Tlm value. 60% survival in 96 hrs.																	
Same as above	6-20-56	100	5	10	24-38 hrs	-	-	100	80	60	60	Initial		-	-	-	-	-	
Oxygenated												96 hrs.		6.2	7.7	98	4	170	
		56	5	10	-	-	-	100	100	100	100	Initial		-	-	-	-	-	
												96 hrs.		5.6	7.8	100	4	155	
		32	5	10	77 hrs.	-	-	100	100	80	80	Initial		-	-	-	-	-	
												96 hrs.		6.0	7.8	96	4	150	
Buffalo River	6-22-56	100	5	10	24 hrs.	-	-	80	80	80	60	Initial	23	3.4	7.2	94	10	190	Light brown
Michigan St.												96 hrs.	23	4.6	7.7	100	6	175	No odor
bridge		56	5	10	-	-	-	100	100	100	100	Initial		5.2	7.5	94	6	160	Slight turbidity
4-Hr.Composite												96 hrs.		4.6	7.7	100	4	160	
In Lab		32	5	10	48 hrs.	-	-	100	80	80	80	Initial		6.8	7.7	94	2	145	
1:00 PM 6-22												96 hrs.		5.6	7.8	100	4	145	
Fish Added		Control	10	20	-	-	-	100	100	100	100	Initial		7.8	8.2	94	0	135	
5:00 PM 6-22												96 hrs.		4.8	7.7	96	4	130	
		No Tlm value. 60% survival in 96 hrs.																	
Same as above	6-22-56	100	5	10	44 hrs.	-	-	100	80	80	80	Initial		-	-	-	-	-	
Oxygenated												96 hrs.		6.4	7.8	-	-	-	
		56	5	10	-	-	-	100	100	100	100	Initial		-	-	-	-	-	
												96 hrs.		6.2	7.8	-	-	-	
		32	5	10	-	-	-	100	100	100	100	Initial		-	-	-	-	-	
												96 hrs.		5.6	7.9	-	-	-	
Buffalo River	11-8-56	100	5	10	-	-	-	100	100	100	100	Initial		1.8	6.8	92	-	225	Light brown
Michigan St.Bridge												96 hrs.		4.6	7.6	-	-	-	Faint gasoline odor
4-Hr.Composite		56	5	10	-	-	-	100	100	100	100	Initial		5.4	7.3	92		165	Slight turbidity
In Lab												96 hrs.		-	-	-	-	-	
11:30 AM 11/8		32	5	10	-	-	-	100	100	100	100	Initial		6.2	7.4	92		170	
Fish Added												96 hrs.		-	-	-	-	-	
10:30 AM 11/9																			
		No Tlm value. 100% survival in 96 hrs.																	